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(54) ELECTRODE FOR LITHIUM SECONDARY BATTERY AND THE LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an electrode for lithium secondary battery of high discharge capacity and superior charging and discharging cycle characteristics, and to provide a lithium secondary battery using the electrode.

SOLUTION: In this electrode for lithium secondary battery, comprising a thin film formed of an active material on a current collector, an alloy thin film (Sn-Co or the like) formed of a metal alloyed with lithium (Sn or the like), a metal which is not alloyed with lithium (Co or the like) is provided on the current collector, such as copper foil or the like, and the metal alloyed with lithium and the metal not alloyed with lithium are preferably in the relation of not forming an intermetallic compound.

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## CLAIMS

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[Claim(s)]

[Claim 1] The electrode for lithium secondary batteries characterized by preparing the alloy thin film which consists of a lithium, a metal to alloy, and a lithium and the metal which is not alloyed on a charge collector.

[Claim 2] The electrode for lithium secondary batteries according to claim 1 characterized by being a lithium, the metal which the metal which is not alloyed alloys with a lithium, and the metal which forms an intermetallic compound.

[Claim 3] The electrode for lithium secondary batteries according to claim 1 or 2 characterized by forming said alloy thin film of plating.

[Claim 4] The electrode for lithium secondary batteries given in any 1 term of claims 1-3 characterized by said alloy thin film being divided into island shape by the break formed in the thickness direction.

[Claim 5] The electrode for lithium secondary batteries according to claim 4 characterized by forming said break by the charge and discharge after the first time.

[Claim 6] The electrode for lithium secondary batteries according to claim 4 or 5 characterized by forming irregularity in said current collection body surface, and dividing said alloy thin film into island shape along with the trough of this irregularity.

[Claim 7] The electrode for lithium secondary batteries given in any 1 term of claims 1-6 characterized by surface roughness Ra of said charge collector being 0.01-2 micrometers.

[Claim 8] The electrode for lithium secondary batteries given in any 1 term of claims 1-6 characterized by surface roughness Ra of said charge collector being 0.01-1

micrometer.

[Claim 9] The electrode for lithium secondary batteries given in any 1 term of claims 1-6 characterized by surface roughness Ra of said charge collector being 0.1-1 micrometer.

[Claim 10] The electrode for lithium secondary batteries given in any 1 term of claims 1-9 characterized by forming said charge collector from copper.

[Claim 11] The electrode for lithium secondary batteries given in any 1 term of claims 1-10 characterized by said charge collector being electrolytic copper foil.

[Claim 12] The electrode for lithium secondary batteries given in any 1 term of claims 1-11 characterized by for a lithium and the metal to alloy being Sn and being the metal with which a lithium and the metal which is not alloyed form Sn and an intermetallic compound.

[Claim 13] The electrode for lithium secondary batteries according to claim 12 characterized by for a lithium and the metal to alloy being Sn and a lithium and the metal which is not alloyed being at least one sort chosen from Fe, Co, and nickel.

[Claim 14] The electrode for lithium secondary batteries given in any 1 term of claims 1-12 in which Co is contained at least as a metal which a lithium and the metal to alloy are Sn and is not alloyed with a lithium and by which it is characterized rattlingly.

[Claim 15] The electrode for lithium secondary batteries according to claim 14 characterized by for a lithium and the metal to alloy being Sn, for a lithium and the metal which is not alloyed being Co(es), and said alloy thin film being a Sn-Co alloy thin film.

[Claim 16] The electrode for lithium secondary batteries according to claim 14 characterized by for a lithium and the metal to alloy being Sn, for a lithium and the metal which is not alloyed being nickel and Co, and said alloy thin film being a Sn-nickel-Co alloy thin film.

[Claim 17] The electrode for lithium secondary batteries given in any 1 term of claims 1-16 characterized by forming the mixolimnion of a current collection body constituent and an alloy content in the interface of said charge collector and said alloy thin film.

[Claim 18] A lithium secondary battery equipped with the negative electrode which becomes any 1 term of claims 1-17 from the electrode of a publication, a positive electrode, and nonaqueous electrolyte.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the lithium secondary battery using the new electrode for lithium secondary batteries and this new.

[0002]

[Description of the Prior Art] In recent years, cell properties, such as charge and discharge voltage, a charge-and-discharge cycle-life property, and a preservation property, are greatly influenced with the electrode with which the lithium secondary battery with which researches and developments are done briskly is used. From this, improvement in a cell property is achieved by improving an electrode active material.

[0003] Although per weight and per volume could constitute the cell of a high energy density when the lithium metal was used as a negative-electrode active material, the lithium deposited in the shape of a dendrite at the time of charge, and there was a problem of causing an internal short circuit.

[0004] On the other hand, the lithium secondary battery using a lithium, the aluminum to alloy, silicon, tin, etc. as an electrode is electrochemically reported in the case of charge (Solid State Ionics, 113-115, p57 (1998)). [0005]

[Problem(s) to be Solved by the Invention] However, when these lithiums (Li) and the metal to alloy are used as a negative-electrode ingredient, a big cubical expansion and contraction arise with the occlusion of a lithium, and emission, and since an electrode active material carries out pulverization and is desorbed from a charge collector, there is a problem that sufficient cycle property is not acquired.

[0006] The purpose of this invention solves these conventional problems, and its

discharge capacity is high and is to offer the lithium secondary battery using the electrode for lithium secondary batteries and this excellent in the cycle property.

[0007]

[Means for Solving the Problem] The electrode for lithium secondary batteries of this invention is characterized by preparing the alloy thin film which consists of a lithium, a metal to alloy, and a lithium and the metal which is not alloyed on a charge collector.

[0008] In this invention, a lithium and the metal to alloy are metals which form alloys, such as a lithium, the solid solution, or an intermetallic compound, and, specifically, Sn, germanium, aluminum, In, Mg, Si, etc. are mentioned.

[0009] In this invention, a lithium and the metal which is not alloyed are metals which do not form alloys, such as a lithium, the solid solution, or an intermetallic compound, and, specifically, is a metal with which an alloy condition does not exist in a binary-condition Fig. with a lithium. As a lithium and a metal which is not alloyed, Cu, Fe, nickel, Co, Mo, W, Ta, Mn, etc. are mentioned, for example.

[0010] As for a lithium and the metal which is not alloyed, in this invention, it is desirable that they are a lithium, the metal to alloy, and the metal which forms an intermetallic compound. Here, an intermetallic compound means the compound which has the specific crystal structure which metals combined by the specific ratio. In this invention, when a lithium and the metal to alloy are Sn, as for a lithium and the metal which is not alloyed, it is desirable that it is the metal which forms Sn and an intermetallic compound. As such a metal, at least one sort chosen from Ti, Mn, Fe, nickel, Co, Cu, Zr, and Mo is mentioned, for example. These metals may be contained independently and may be contained. [ two or more ] It is desirable that it is at least one sort especially chosen from Fe, Co, and nickel also in these, and it is desirable that Co is contained especially at least. In addition, in this invention, the alloy thin film which consists of these metals does not necessarily need to form the intermetallic compound of these metals into a thin film. Therefore, an alloy thin film does not need to be crystallinity, for example, may be the compound of an amorphous \*\* unfixed ratio.

[0011] In this invention, the thin film of the alloy which consists of a lithium, a metal to alloy, and a lithium and the metal which is not alloyed is prepared on a charge collector. Moreover, although especially the approach of forming an alloy thin film is not limited, electrochemical approaches, such as electrolytic plating and electroless deposition, are used preferably. Moreover, an alloy thin film may be formed by the physical thin film forming methods, such as a CVD method, the sputtering method, a vacuum deposition method, and a spraying process.

[0012] Especially if the charge collector used by this invention is a charge collector

which can be used for the electrode for lithium secondary batteries, it is not limited, and the metallic foil which consists of copper, nickel, titanium, iron, stainless steel, molybdenum, cobalt, chromium, tungsten, tantalum, silver, etc. can be used for it.

[0013] In this invention, it is desirable that irregularity is formed on the surface of a charge collector. Although especially the upper limit of surface roughness Ra of a charge collector is not restricted, since that to which surface roughness Ra exceeds 2 micrometers is generally hard to come to hand as copper foil of thickness practical as a cell, as an upper limit of the desirable range of surface roughness Ra, it is 2 micrometers or less, and is 1 micrometer or less still more preferably. Moreover, as for the lower limit of surface roughness Ra, it is desirable that it is 0.01 micrometers or more. Therefore, the desirable range of surface roughness Ra is 0.01-2 micrometers, and is 0.01-1 micrometer still more preferably.

[0014] Surface roughness Ra is set to Japanese Industrial Standards (JIS B 0601-1994), for example, can be measured with a surface roughness meter. When surface roughness Ra uses big copper foil as a charge collector, it is desirable to use electrolytic copper foil.

[0015] As for an alloy thin film, in this invention, it is desirable that the break formed in the thickness direction separates into island shape. A charge-and-discharge cycle property can be remarkably raised by separating into island shape, after the alloy thin film has stuck with the charge collector.

[0016] Since an alloy thin film contains a lithium and the metal to alloy, it can alloy and carry out occlusion of the lithium in the case of a charge-and-discharge reaction. For example, when using the electrode of this invention as a negative electrode, in the case of charge, occlusion of the lithium is carried out into an alloy thin film, and a lithium is emitted from an alloy thin film in the case of discharge. The volume of an alloy thin film is expanded and contracted by the occlusion and emission of such a lithium. Even if it expands and contracts the volume in case an alloy thin film is a charge-and-discharge reaction since space is established in the surroundings of it by dividing the alloy thin film into island shape, the volume change is absorbable in a surrounding space part. Therefore, distortion is not produced inside an alloy thin film and the exfoliation from the pulverization and the charge collector of an alloy thin film can be controlled.

[0017] If an alloy thin film is formed on a charge collector by plating or the physical thin film formation approach, an alloy thin film will be formed as a continuous thin film. In such a case, the break of the above-mentioned thickness direction is usually formed of the charge-and-discharge reaction after the first time. That is, in case it contracts after

an alloy thin film expands in a charge-and-discharge reaction, the break of the above-mentioned thickness direction is formed and an alloy thin film is divided into island shape. The separation by the break of such a thickness direction becomes that it is easy to be formed especially when the charge collector which has irregularity is used for a front face. Formation of an alloy thin film forms the shape of tothing also along the irregularity of a current collection body surface or the front face of an alloy thin film on the charge collector which has irregularity on a front face. If such an alloy thin film carries out expansion contraction, a break will be formed in the thickness direction by the line which connects the trough of the irregularity of an alloy thin film front face, and the trough of the irregularity of a current collection body surface, and it will be thought that an alloy thin film is divided into island shape along with the trough of the irregularity of a current collection body surface.

[0018] As for the lithium in an alloy thin film, and the amount of the metal which is not alloyed, in this invention, it is desirable that it is 50% or less as a mole ratio (atomic ratio). If it increases more than this, since the amount of a lithium and the metal to alloy will decrease relatively, charge-and-discharge capacity becomes low in connection with this and is not desirable. Moreover, as for the amount of a lithium and the metal which is not alloyed, it is desirable in an alloy thin film that it is 0.1% or more as a mole ratio (atomic ratio). By containing a lithium and the metal which is not alloyed, expansion and contraction of the charge-and-discharge reaction of an alloy thin film of the volume in the case can be restricted, and a charge-and-discharge cycle property can be raised as this result. Therefore, as for the viewpoint of the improvement in a cycle property to a lithium, and the metal which is not alloyed, being contained 0.1% or more is desirable. Therefore, the lithium in an alloy thin film and the range of the desirable content of the metal which is not alloyed are 0.1 - 50% as a mole ratio (weight ratio). The range of a still more desirable content is 1 - 40% as a mole ratio (atomic ratio).

[0019] In this invention, the mixolmion of a current collection body constituent and an alloy content may be formed in the interface of a charge collector and an alloy thin film. By forming such a mixolmion, the adhesion of the alloy thin film to a charge collector can be raised, and improvement in the further cycle property can be expected. Such a mixolmion can be formed by performing heat treatment etc., after forming an alloy thin film on a charge collector. It is desirable that it is temperature lower than the melting point of an alloy thin film and the melting point of a charge collector as temperature of heat treatment.

[0020] The lithium secondary battery of this invention is characterized by having the negative electrode which consists of an electrode for lithium secondary batteries of



above-mentioned this invention, a positive electrode, and nonaqueous electrolyte. Although especially the solvent of the electrolyte used for the lithium secondary battery of this invention is not limited, the mixed solvent of annular carbonate, such as ethylene carbonate, propylene carbonate, butylene carbonate, and vinylene carbonate, and chain-like carbonate, such as dimethyl carbonate, methylethyl carbonate, and diethyl carbonate, is illustrated. Moreover, the mixed solvent of said annular carbonate and ether system solvents, such as 1, 2-dimethoxyethane, 1, and 2-diethoxy ethane, is also illustrated. Moreover, as an electrolytic solute, those mixture, such as  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiCF}_3\text{SO}_3$ , and  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ,  $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)$ ,  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ ,  $\text{LiC}(\text{C}_2\text{F}_5\text{SO}_2)_3$ , is illustrated. Furthermore, inorganic solid electrolytes, such as a gel polymer electrolyte which sank the electrolytic solution into polymer electrolytes, such as polyethylene oxide and a polyacrylonitrile, and  $\text{LiI}$ ,  $\text{Li}_3\text{N}$ , are illustrated as an electrolyte. The electrolyte of the lithium secondary battery of this invention can be used without constraint, unless Li compound as a solute which makes ion conductivity discover, and the solvent which dissolves and holds this decompose on the electrical potential difference at the time of charge of a cell, discharge, or preservation.

[0021] As positive active material of the lithium secondary battery of this invention, lithium content transition-metals oxide, such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiMnO}_2$ ,  $\text{LiCo}_{0.5}\text{nickel}_{0.5}\text{O}_2$ , and  $\text{LiNi}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1}\text{O}_2$ , and the metallic oxide which does not contain lithiums, such as  $\text{MnO}_2$ , are illustrated. Moreover, in addition to this, if it is the matter electrochemically inserted and desorbed from a lithium, it can use without a limit.

[0022]

[Embodiment of the Invention] It is possible to change this invention suitably in the range which is not limited to the following examples at all and does not change the summary, and to carry out hereafter, although this invention is further explained to a detail based on an example.

[0023] (Experiment 1)

[Production of an electrode] The thin film which consists of a Sn-Co alloy with a thickness of 2 micrometers was formed with electrolysis plating on electrolytic copper foil (surface roughness  $R_a=0.188\text{micrometer}$ ) with a thickness of 18 micrometers. As a plating bath, the plating bath which mixed chlorination tin, a cobalt chloride, a sodium chloride, a hydrochloric acid, ethylene glycol, and thiourea was used.

[0024] After forming a Sn-Co alloy thin film, it cut off in  $2\text{cm}\times 2\text{cm}$  magnitude, and considered as the electrode a1. The slurry which mixed the fluoro-resin (PVdF) with the

alloy powder (mole ratio 8:2) of Sn and Co produced by the atomizing method by the weight ratio of 95:5 as a comparison was prepared, and after applying this slurry on electrolytic copper foil and drying, it cut off in 2cmx2cm magnitude, and considered as the electrode b1.

[0025] [Production of the electrolytic solution] LiPF<sub>6</sub> [ one mol / /] was dissolved in the mixed solvent of the volume ratio 1:1 of ethylene carbonate and diethyl carbonate 1., and the electrolytic solution was produced.

[0026] [Production of a beaker cel] The beaker cel as shown in drawing 3 was produced using the above-mentioned electrodes a1 and b1 as an operation pole. As shown in drawing 3 , the beaker cel is constituted by immersing a counter electrode 3, the operation pole 4, and the reference pole 5 into the electrolytic solution into which it was put in the container 1. The lithium metal was used as a counter electrode 3 and a reference pole 5, using the above-mentioned electrolytic solution as the electrolytic solution 2.

[0027] [Measurement of a cycle property] the beaker cel produced as mentioned above 25 degrees C performs constant-current charge to 0V (vs.Li/Li+) by 0.2mA, respectively, perform constant-current discharge to 2V (vs.Li/Li+) by 0.2mA after that, and this is made into 1 cycle. Charge and discharge were performed up to 10 cycles, the charge capacity and discharge capacity per unit active material weight in each cycle were measured, and it asked for the initial effectiveness and the capacity maintenance factor which are defined as the following formulas. A result is shown in Table 1. In addition, reduction of an operation pole is considered as charge and oxidation of an operation pole is considered as discharge here.

[0028] Initial effectiveness (%) =(charge capacity of discharge capacity / 1 cycle eye of 1 cycle eye) x100 capacity maintenance-factor (%) =(discharge capacity of discharge capacity / 1 cycle eye of 10 cycle eye) x100[0029]

[Table 1]

電極	1サイクル目の 充電容量 (mAh/g)	1サイクル目の 放電容量 (mAh/g)	初期効率 (%)	10サイクル目の 放電容量 (mAh/g)	容量維持率 (%)
a 1	7 7 2	6 3 2	8 2	6 2 8	9 9
b 1	4 0 3	3 0 9	7 7	3	1

[0030] Compared with the comparative electrode b1, it has a high charge-and-discharge capacity, and the electrode a1 according to this invention shows the good cycle property so that clearly from the result shown in Table 1.

[0031] (Experiment 2) Using the electrodes a1 and b1 obtained in the experiment 1 as a negative electrode, the lithium secondary battery was produced and the charge-and-discharge cycle property was evaluated.

[0032] [Production of a positive electrode] 85 % of the weight of  $\text{LiCoO}_2$  powder with a mean particle diameter of 10 micrometers, 10 % of the weight of carbon powder as an electric conduction agent, and 5 % of the weight of polyvinylidene fluoride powder as a binder were mixed, N-methyl pyrrolidone was added and kneaded into the obtained mixture, and the slurry was produced. After applying this slurry to one side of aluminium foil with a thickness of 20 micrometers with the doctor blade method and drying, it cut off in 2cmx2cm magnitude, and the positive electrode was produced.

[0033] [Production of a cell] After inserting the positive electrode obtained as mentioned above and electrodes a1 or b1 in the sheathing object which consists of lamination and a laminate material made from aluminum through the fine porosity film made from polyethylene, 500microl impregnation of the electrolytic solution same with having produced in the experiment 1 was done into this, and the lithium secondary battery was produced.

[0034] Drawing 4 is the top view showing the produced lithium secondary battery. As shown in drawing 4 , through the separator 12 which consists of fine porosity film made from polyethylene, a positive electrode 11 and a negative electrode 13 are put together, and it is inserted into the sheathing object 14. After inserting in the sheathing object 14, the electrolytic solution is poured in and the lithium secondary battery is produced by closing by closure section 14a of the sheathing object 14.

[0035] Drawing 5 is a sectional view to show the combination condition of the electrode in the interior of a cell. As shown in drawing 5 , it is combined so that a positive electrode 11 and a negative electrode 13 may counter through a separator 12. On positive-electrode charge collector 11b which consists of aluminum in a positive electrode 11, positive-active-material layer 11a is prepared, and this positive-active-material layer 11a is in contact with the separator 12. Moreover, in the negative electrode 13, negative-electrode active material layer 13a is prepared on negative-electrode charge collector 13b which consists of copper, and this negative-electrode active material layer 13a is in contact with the separator 12. In this example, negative-electrode active material layer 13a is the layer formed from the Sn-Co alloy thin film.

[0036] As shown in drawing 4 , positive-electrode tab 11c which consists of aluminum for external ejection is attached in positive-electrode charge collector 11b. Moreover, negative-electrode tab 13c set also to negative-electrode charge collector 13b from the

nickel for external ejection is attached.

[0037] In the produced lithium secondary battery, what used the electrode a1 for the negative electrode was used as the cell A1, and the thing using an electrode b1 was used as the cell B1. The design capacity of each cell was 6mAh.

[0038] [Charge and discharge test] The charge and discharge test was performed about the cells A1 and B1 produced as mentioned above. Charge was performed until charge capacity was set to 6mAh(s) by 1.2mA constant current, discharge was performed to 2.0V by 1.2mA constant current, and this was made into 1 cycle. However, charge of 1 cycle eye (first time) was performed until charge capacity reached 7.2mAh(s). It asked for initial effectiveness and a capacity maintenance factor like the above-mentioned experiment 1. A result is shown in Table 2. In addition, measurement was performed at 25 degrees C.

[0039]

[Table 2]

[0040] The cell A1 according to this invention shows the good charge-and-discharge cycle property so that clearly from the result shown in Table 2. Drawing 1 is a scanning electron microscope photograph when observing the front face of the electrode a1 picked out from the cell A1 of 10 cycle eye in the charge and discharge test. It is 1000 times the scale factor of this. Drawing 2 is a scanning electron microscope photograph when slicing, after carrying out embedding of this electrode a1 by resin, and observing a cross section. It is 5000 times the scale factor of this. drawing 1 and drawing 2 -- since -- in the electrode a1 after a charge-and-discharge reaction, the break formed in the thickness direction of an alloy thin film shows that the alloy thin film is divided into island shape so that clearly. This break is formed along with the trough of the irregularity of a current collection body surface so that clearly from drawing 2 . Moreover, it turns out that this break stands in a row in the shape of a mesh along with the trough of the irregularity of a current collection body surface in the direction of a film surface of an alloy thin film so that clearly from drawing 1 .

[0041] The alloy thin film is formed along with the irregularity of a current collection body surface, and the break is formed along with the line which connects the trough of

the irregularity of an alloy thin film front face, and the trough of the irregularity of a current collection body surface so that clearly from drawing 2 . Such a break is considered to have been formed when an alloy thin film expanded and contracted by the charge-and-discharge reaction.

[0042] Since space exists in the perimeter of an island-shape alloy thin film as shown in drawing 1 and drawing 2 , he can absorb the volume change in the case of the charge-and-discharge reaction of an alloy thin film, and it is thought by such space that a good cycle property can be shown by it.

[0043] Although the Sn-Co alloy thin film is formed with electrolysis plating in the above-mentioned example on the substrate which is a charge collector, you may form by the electroless deposition method. Furthermore, you may form by the thin film formation approaches, such as the sputtering method, a vacuum deposition method, and a spraying process.

[0044] (Experiment 3) The thin film which consists of a Sn-nickel alloy with a thickness of 2 micrometers, a Sn-Fe alloy, a Sn-Pb alloy, and a Sn-Zn alloy was formed with electrolysis plating like the experiment 1 on electrolytic copper foil (surface roughness  $R_a=0.188$ micrometer) with a thickness of 18 micrometers.

[0045] The Sn-nickel alloy thin film was formed using the Sn-nickel plating bath which mixed a potassium pyrophosphate, tin chloride, the nickel chloride, and the glycine. The Sn-Fe alloy thin film was formed using the Sn-Fe plating bath which mixed chlorination tin, an iron sulfate, a sodium citrate, and L-ascorbic acid. In addition, two kinds of plating baths from which a presentation differs were used for the Sn-Fe plating bath.

[0046] The Sn-Pb alloy thin film was formed using the Sn-Pb plating bath which mixed HOUFUTSU-ized tin, HOUFUTSU-ized lead, fluoroboric acid, the boric acid, and the peptone. The Sn-Zn alloy thin film was formed using the Sn-Zn plating bath which mixed organic-acid tin, organic-acid zinc, and a complexing agent.

[0047] The electrode in which the Sn-nickel alloy thin film was formed was used as this invention electrode c1, the electrode in which the Sn-Fe alloy thin film was formed was used as this invention electrodes c2 and c3, the electrode in which the Sn-Pb alloy thin film was formed was used as the reference electrode e1, and the electrode in which the Sn-Zn alloy thin film was formed was used as the reference electrode e2. In addition, nickel and Fe are a lithium and a metal which is not alloyed, and Sn, Pb, and Zn are a lithium and a metal to alloy. Therefore, a Sn-nickel alloy thin film and a Sn-Fe alloy thin film are alloy thin films according to this invention, and a Sn-Pb alloy thin film and a Sn-Zn alloy thin film are alloy thin films of this invention out of range.

[0048] The presentation ratio of the alloy in the alloy thin film formed in this invention

electrodes c1-c3 and reference electrodes e1 and e2 was analyzed by ICP emission spectrochemical analysis. The presentation ratio of an alloy thin film is shown in Table 3. In addition, in Table 3, the presentation ratio of the alloy thin film in this invention electrode a1 produced in the experiment 1 is also shown collectively.

[0049]

[Table 3]

[0050] Reference electrodes e1 and e2 were used for this invention electrode c1 - c3 list as an operation pole, the beaker cel was produced like the experiment 1, and the cycle property was evaluated. An evaluation result is shown in Table 4.

[0051]

[Table 4]

[0052] this invention electrodes c1-c3 show the good cycle property compared with reference electrodes e1 and e2 so that clearly from the result shown in Table 4.

[0053] (Experiment 4) The thin film which consists of a Sn-Co alloy with a thickness of 2 micrometers was formed on electrolytic copper foil like the experiment 1 using two kinds of electrolytic copper foil (thickness of 18 micrometers) with which surface

roughness Ra differs, and the electrode was produced.

[0054] The electrode using the electrolytic copper foil whose surface roughness Ra is 0.188 micrometers was used as this invention electrode d1, and the electrode using the electrolytic copper foil whose surface roughness Ra is 1.19 micrometers was used as this invention electrode d2. Moreover, surface roughness Ra formed the thin film which consists of a Sn-Co alloy with a thickness of 2 micrometers similarly also on the rolling copper foil which is 0.04 micrometers, and considered as this invention electrode d3. In addition, this invention electrode d1 is the same as the electrode a1 shown in Table 1.

[0055] Using this invention electrodes d1, d2, and d3, a beaker cel is produced like experiment 1 and the evaluation result of having evaluated the charge-and-discharge cycle property is shown in Table 5.

[0056]

[Table 5]

[0057] Although a good cycle property is acquired also when surface roughness Ra of a charge collector exceeds 1 micrometer so that clearly from the result shown in Table 5, surface rough Ra of a charge collector is understood that 1 micrometer or less is more desirable. Moreover, the cycle property with this invention electrode d1 better than this invention electrode d3 is acquired. Therefore, especially as surface roughness Ra of a charge collector, it turns out that the range of 0.1-1 micrometer is desirable.

[0058] (Experiment 5) The thin film which consists of a Sn-nickel-Co alloy with a thickness of 2 micrometers was formed with electrolysis plating like the experiment 1 on electrolytic copper foil (surface roughness Ra=0.188micrometer) with a thickness of 18 micrometers.

[0059] The Sn-nickel-Co alloy thin film was formed using the Sn-nickel-Co plating bath which mixed a potassium pyrophosphate, tin chloride, the nickel chloride, and the cobalt chloride. Using the obtained this invention electrode f1, the beaker cel was produced like the experiment 1 and the cycle property was evaluated. An evaluation result is shown in Table 6. Moreover, the chemical composition of the plating film formed in the electrode is shown in Table 7.

[0060]

[Table 6]

[0061]

[Table 7]

[0062] The electrode f1 in which the Sn-nickel-Co alloy thin film was formed has a high charge-and-discharge capacity, and shows the cycle property better than the electrode c1 using a Sn-nickel alloy thin film so that clearly from the result shown in Table 6.

[0063]

[Effect of the Invention] According to this invention, discharge capacity is high and can consider as the lithium secondary battery excellent in the cycle property.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] The scanning electron microscope photograph in which the front face of the electrode a1 of the example according to this invention is shown.

[Drawing 2] The scanning electron microscope photograph in which the cross section of the electrode a1 of the example according to this invention is shown.

[Drawing 3] The typical sectional view showing the beaker cell produced in the example.

[Drawing 4] The top view showing the lithium secondary battery produced in the example.

[Drawing 5] The sectional view showing the combination structure of the electrode in the lithium secondary battery shown in drawing 4 .

[Description of Notations]

- 1 -- Container
- 2 -- Electrolytic solution
- 3 -- Counter electrode
- 4 -- Operation pole
- 5 -- Reference pole
- 11 -- Positive electrode
- 11a -- Positive-active-material layer
- 11b -- Positive-electrode charge collector
- 11c -- Positive-electrode tab
- 12 -- Separator
- 13 -- Negative electrode
- 13a -- Negative-electrode active material layer
- 13b -- Negative-electrode charge collector
- 13c -- Negative-electrode tab
- 14 -- Sheathing object
- 14a -- The closure section of a sheathing object